

Os ISOTOPIC COMPOSITION AND CONCENTRATION IN THE OCEANS: TERRESTRIAL AND EXTRATERRESTRIAL SOURCES.

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The Os isotopic composition and concentration of seawater can be used to put limits on the input of extraterrestrial and continental material. This is because of large isotopic differences in $^{187}\text{Os}/^{186}\text{Os}$ between extraterrestrial sources and the earth's crust. Typically, $^{187}\text{Os}/^{186}\text{Os} \sim 1.0$ in chondritic meteorites [$^{187}\text{Re}/^{186}\text{Os} \sim 3$; average $[\text{Os}] = 2.6 \text{ nm g}^{-1}$ (1)] and $^{187}\text{Os}/^{186}\text{Os} \sim 10.5$ in continental crustal rocks [$^{187}\text{Re}/^{186}\text{Os} \sim 400$; average $[\text{Os}] = 0.26 \text{ pm g}^{-1}$ (2)]. However, Os is one of the rarest elements in seawater. Analytical difficulties have previously prevented direct measurement of Os in seawater. We report Os data in waters from the Atlantic and Pacific oceans. Several indirect determinations of the Os isotopic composition of seawater have been reported. Early experiments used marine Mn-nodules (3-6) and abyssal red clays (7). The results suggested widely varying $^{187}\text{Os}/^{186}\text{Os}$ ratios (5 to 11) between and within different ocean basins. These data were strongly influenced by sources of Os other than seawater (8, 9). Recent studies used: (a) bulk analyses of rapidly accumulating metalliferous carbonates (10); (b) extensive leaching procedures to remove selectively "hydrogenous" Os from organic-rich marine sediments (8); and (c) hydrogenous Fe-Mn crusts (11). These studies suggest that the present-day $^{187}\text{Os}/^{186}\text{Os}$ of seawater varies between 7.9 and 8.8. However, the sediments/leaches may contain labile Os derived from multiple sources (12, 13) and thus the inferences from sediment data about seawater are uncertain. A preliminary attempt to measure directly Os in a seawater sample yielded highly uncertain values of $^{187}\text{Os}/^{186}\text{Os} = 6.3 \pm 3.1$ and $[\text{Os}] = 9 \pm 4.5 \text{ fm l}^{-1}$ (14). None of these studies has established the Os isotopic composition and concentration of seawater.

Advances in negative thermal ionization mass spectrometry (NTIMS; 15, 16) and in chemical procedures have made it possible to measure Re and Ir in seawater (17, 18). Following on the work by Anbar *et al.* (18), we have developed a procedure to preconcentrate Os quantitatively (~90%) from seawater. The samples are then processed using the chemical procedures developed for meteorites (19, 20). This method permits the analysis of Os in 1-10 kg of seawater and may be applicable to other natural waters. The total procedural Os blank is 8 fm and is about 10% of the total Os in a 4 kg seawater sample. Note that although a typical uncertainty in the measured $^{187}\text{Os}/^{186}\text{Os}$ is about 1%, an uncertainty of 25% in the blank introduces ~5% uncertainty in the corrected $^{187}\text{Os}/^{186}\text{Os}$. Four samples were chosen of water from the

Pacific and Atlantic oceans. These samples were collected from the (a) Central Pacific (22° 45'N, 158° W); (b) North-East Pacific (Juan de Fuca ridge); and (c) two Atlantic samples in a depth profile near Bermuda (31° 50'N, 64° 10'W). The results are listed in Table 1. The Os concentration ranges from 15 to 19 fm kg⁻¹. This is much higher than the diverse guesses/estimates in the literature. The directly determined $^{187}\text{Os}/^{186}\text{Os}$ ratio of the deep ocean waters that are least affected by hydrothermal activity or terrigenous influx is 8.0 ± 0.1 and does not appear to vary between the Pacific and Atlantic Oceans. Note that $^{187}\text{Os}/^{186}\text{Os}$ at the Juan de Fuca ridge site is 7.0 ± 0.07 .

The data may be used to obtain an estimate of the mean life of dissolved Os in seawater which is defined as $\bar{\tau}_{\text{Os}} = N_{\text{Os}}^{\text{sw}} / J_{\text{Os}}^{\text{out}}$. Here $N_{\text{Os}}^{\text{sw}}$ is the number of Os atoms in the oceans and $J_{\text{Os}}^{\text{out}}$ is the Os burial flux. For a steady state model for Os in seawater (SW), with dissolved inputs from continents (C), cosmic dust (D) and hydrothermal sources (H), we obtain:

$$f_{186\text{Os}}^{\text{C}} \equiv J_{186\text{Os}}^{\text{C}} / \left(N_{186\text{Os}}^{\text{sw}} / \bar{\tau}_{\text{Os}} \right) \approx \frac{(R^{\text{SW}} - R^{\text{D}})}{(R^{\text{C}} - R^{\text{D}})}$$

where $R^j = (^{187}\text{Os}/^{186}\text{Os})^j$ in the dissolved component from each source j ($j = \text{SW}, \text{C}, \text{D}, \text{H}$). Here $f_{186\text{Os}}^{\text{C}}$ is the ratio of dissolved Os input from continents to the total dissolved Os input. We assumed $R^{\text{H}} \approx R^{\text{D}}$. From the data we find that $f_{186\text{Os}}^{\text{C}} \approx 0.74$. Thus 74% of the dissolved Os in the oceans derives from the continents and 26% derives from the sum of dissolved cosmic dust plus hydrothermal sources. This is in accord with estimates of Pegram *et al.* (21). If we consider the ratio of Ir/Os (r^j) to be the same as in their sources contributing to the dissolved load, then we obtain

$$\bar{\tau}_{\text{Os}} / \bar{\tau}_{\text{Ir}} = \frac{(r^{\text{C}} - r^{\text{D}})f_{186\text{Os}}^{\text{C}} + (1 - f_{186\text{Os}}^{\text{H}})R^{\text{D}} + R^{\text{H}}f^{\text{H}}}{r^{\text{SW}}}$$

where $\bar{\tau}_{\text{Ir}}$ is the mean oceanic residence time of Ir and $f_{186\text{Os}}^{\text{H}}$ is the ratio of dissolved Os input from hydrothermal sources to the total dissolved Os input. Using our concentration data for Os and those of Anbar *et al.* (18) for Ir, it follows that $\bar{\tau}_{\text{Os}} / \bar{\tau}_{\text{Ir}} \geq 20$.

Anbar *et al.* (18) have estimated that ~70% of the Ir in seawater is from the continents and that $2 \times 10^4 \text{ y} \geq \bar{\tau}_{Ir} \geq 2 \times 10^3 \text{ y}$. It follows that $4 \times 10^5 \text{ y} \geq \bar{\tau}_{Os} \geq 4 \times 10^4 \text{ y}$. Here the lower limit is reasonably reliable. The upper limit is quite uncertain. Nonetheless, this would indicate that the Os residence time in the oceans is quite long, so that perturbations due to a sudden input will take a substantial time to damp out. This also suggests that gradients in $^{187}\text{Os}/^{186}\text{Os}$ may get set-up in the oceans at the ridges with hydrothermal activity. For example, the $^{187}\text{Os}/^{186}\text{Os}$ of the ambient seawater around the Juan de Fuca ridge, where extensive hydrothermal activity is underway, appears to have been lowered by about 10% (Table 1). A longer oceanic residence time of Os is in contrast to many of the previous estimates of the Os residence time. From our results we expect that the dissolved load of Os in river waters is quite high (15-150 fm kg^{-1}).

We note that the attempts to identify "hydrogenous" Os in modern marine sediments (8-11) appear to give $^{187}\text{Os}/^{186}\text{Os}$ that is approximately the same as our direct determination in seawater. This suggests that the efforts to construct the Os isotopic evolution of seawater using the "hydrogenous" Os in deep marine sediment core-samples (e.g., 13) may be justified. In this context, it is interesting to note that following the K-T impact, a slow recovery of seawater $^{187}\text{Os}/^{186}\text{Os}$ over a period of 3-5 myr as observed by Peucker-Ehrenbrink *et al.* (13) is consistent with the relatively long residence time of Os established here. The wide variability ($\times 10$) of Ir/Os in marine sediments (e.g., 13, 22, 23) is a problem, however, that requires clarification as it may reflect great mobility of Os and/or Ir (see 24). This issue is of

critical importance in using the Os data to estimate the cosmic dust flux over past geologic epochs as well as in the interpretation of $^{187}\text{Os}/^{186}\text{Os}$ in hydrogenous portions of the sediments.

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Table 1.

Sample Location	Depth (m)	Weight (kg)	[Os] fm $\text{kg}^{-1} \pm$	$(^{187}\text{Os}/^{186}\text{Os})_m$	$(^{187}\text{Os}/^{186}\text{Os})_c \pm$
Pacific Ocean					
Central Pacific	3000	10.5	19.0 ± 0.10	7.2 ± 0.06	8.0 ± 0.07
Central Pacific (duplicate)				7.2 ± 0.09	8.0 ± 0.10
Juan de Fuca Ridge	1764	4.1	14.7 ± 0.06	6.3 ± 0.06	7.0 ± 0.07
Atlantic Ocean					
Bermuda†	25	3.7	15.1 ± 2.2		
Bermuda†	3000	4.0	19.1 ± 0.9	6.8 ± 0.5	7.4 ± 0.5
Bermuda	3000	4.1	14.9 ± 0.04	7.1 ± 0.04	7.9 ± 0.04

‡ Blank corrected using $[\text{Os}] = 7.7 \pm 1.9 \text{ fm}$ with $^{187}\text{Os}/^{186}\text{Os} = 1.27 \pm 0.04$. Note 1 fm = 6.02×10^8 atoms. The uncertainty of 25% in blank would contribute ~5% to the uncertainty in $(^{187}\text{Os}/^{186}\text{Os})_c$ and less than 2.5% to the uncertainty in the Os concentration.† Initial low precision measurements.